# ABSTRACT

Pozzolanic reactions play a key role in improving the compressive strengths of compacted fly ash-lime specimens. Based on studies performed with cement amended fly ash (FA), activation of fly ash-lime pozzolanic reactions should accelerate the rate of strength development and mobilize larger compressive strengths facilitating improved engineering performance of fly ash amended materials. Further, use of phosphogypsum (PG) is a cause of environmental concern as the material is acidic (pH < 3.0) and contains considerable amounts of fluoride (0.86%). The main research objectives of the thesis are to activate lime-fly ash reactions by thermal and chemical activation process and examine the efficacy of fly ash pozzolanic reactions in controlling fluoride release by phosphogypsum.

A comprehensive laboratory experimental program was performed to examine the influence of curing temperature (thermal activation) and calcined PG addition (chemical activation) on lime-fly ash reactions. The kinetics of fly ash-lime reactions are examined by monitoring the reacted lime content as function of curing period and temperature. The influence of variations in fly ash/lime content and dry density on the compressive strength developed by specimens is evaluated. The thermodynamic parameters for the fly ash-lime (FA-L) reactions have been delineated. Fly ash-lime-phosphogypsum (FA-L-G) mixes in slurry and compacted states were monitored for fluoride released as function of curing period

The influence of curing temperature in activating fly ash-lime reactions is first examined. Specimens were cured at 25°C (termed RTC or room temperature cured) and at 80° (termed SC or steam cured) to understand thermal activation of fly ash-lime reactions.

The rate of lime consumption by SC specimens classified as 2 stage process. The robust increase during stage 2 of steam curing suggested that the lime-solidification reactions did not reach equilibrium even after 4 days of curing at the elevated temperature. While only 3.1 to 3.3 % of added lime was consumed after 28 days of curing at room temperature, much larger amounts of lime ( 8.6-9.3%) were consumed after 4 days of steam-curing. Further, the lime-fly ash reactions were accelerated by 6 to 7 folds on curing the specimens at elevated temperature. The results indicated that activation of lime-fly ash reactions by curing at elevated temperature besides accelerating the rate of strength development also facilitated development of larger strength.

Analysis of the free energy change values ($\Delta G°$) indicated that the lime solidification reaction alters from dis-favored (less spontaneous) to favoured (spontaneous) state on curing at 80$^{o}$C. The positive $\Delta H°$ (enthalpy change) values for the fly ash-lime reactions indicated that the reactions are endothermic in nature and are facilitated by increase in curing temperature.

Gypsum activation was achieved by addition of 2.5 to 5% calcined phosphogypsum to fly ash lime mixes and curing the compacted specimens at room temperature (FA-L-G specimens). The rate of lime consumption by FA-L-G specimens appeared to be three stage process. The mass of lime consumed by FA-L-G specimens was about 1.5 to 3 folds higher than values of the RTC and SC specimens. Additional lime is consumed by FA-L-G specimens in ettringite formation. A similarity existed between rate of lime consumed and rate of strength developed by the FA-L-G specimens. It is proposed that besides lime solidification reactions, densification of the matrix by filling up of voids by fine gypsum particles and compaction of matrix by the growth of ettringite crystals also contribute to compressive strength of FA-L-G specimens; this additional mechanism of strength development accounts for their higher compressive strength in comparison to the SC and RTC specimens despite similar initial lime addition values. The trend of results suggests that activation of FA-L reactions by calcined PG addition is more effective than steam curing. Comparison of $\Delta G°$ values of RTC, SC and FA-L-G specimens revealed that the spontaneity of the lime solidification reactions is least for RTC specimens and improves with addition of phosphogypsum and further improves on curing at elevated temperature. Fly ash-lime pozzolanic reactions substantially reduced the fluoride released from the FA-L-G specimens. The marked reduction in fluoride released by PG amended with fly ash and lime is ascribed to entrapment of PG particles in the cemented matrix formed by fly ash-lime pozzolanic reactions together with consumption of fluoride in formation of insoluble fluoride bearing compounds.

The thesis brings out that activation of fly ash-lime reactions leading to quicker and larger compressive strength development is achieved by curing the compacted fly ash-lime specimens at 80°C for 24 hr or by addition of 2.5 to 5% of calcined PG to fly ash-lime mix and curing the compacted specimens at room-temperature. As larger strengths are developed by PG addition than by curing at $80^{o}$C, it is recommended that FA-L-G technique be adopted for manufacture of building materials in the civil engineering industry. This technique is also sustainable as it does not require energy for heating which is needed in the steam-curing technique.